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PATENT ABSTRACTS OF JAPAN

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(54) PRODUCTION OF HYDROGENATED PETEROLEUM RESIN AND HYDROGENATING CATALYST USED FOR THE SAME PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for producing a 9C-based hydrogenated petroleum resin good in color tone and heat stability even when the hydrogenation is carried out by suppressing the hydrogenation ratio of the aromatic ring in the 9C-based petroleum resin to about 5-80%.

SOLUTION: A catalyst containing nickel and diatomaceous earth and satisfying conditions of ≥ 48 wt.% nickel content, ≥ 290 m²/g catalyst surface area and ≤ 0.35 g/mL bulk specific gravity is used as a hydrogenating catalyst, in a method for hydrogenating a 9C-based petroleum resin in the presence of the hydrogenating catalyst and producing a 9C-based hydrogenated petroleum resin.

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of C9 system hydrogenation petroleum resin characterized by using what comes to contain nickel and diatomaceous earth, and fulfills 48 % of the weight or more of nickel contents, more than catalyst surface area of 290m²/g, and conditions with a bulk specific gravity of 0.35g [/ml] or less as a hydrogenation catalyst in the approach of hydrogenating C9 system petroleum resin under existence of a hydrogenation catalyst, and manufacturing C9 system hydrogenation petroleum resin.

[Claim 2] The manufacture approach according to claim 1 which hydrogenates 5% or more of the ring of C9 system petroleum resin.

[Claim 3] The manufacture approach according to claim 1 which hydrogenates 40 – 80% of the ring of C9 system petroleum resin.

[Claim 4] The manufacture approach according to claim 1 to 3 of performing hydrogenation using the successive reaction equipment of the fluid bed.

[Claim 5] The hydrogenation catalyst of C9 system petroleum resin which comes to contain the nickel and diatomaceous earth which are used for the manufacture approach of claims 1–4, and fulfills conditions with a bulk specific gravity of 0.35g [/ml] or less 48 % of the weight or more of nickel contents, and more than catalyst surface area of 290m²/g.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of C9 system hydrogenation petroleum resin. C9 system hydrogenation petroleum resin obtained by this invention has a color tone and good thermal stability, and they can use it for tackifiers, such as encapsulant of ** and adhesives, a coating, printing ink, traffic marking paint, and a semi-conductor, a waterproof grant agent, and a pan at a plastics modifier etc.

[0002]

[Description of the Prior Art] C9 system petroleum resin is thermoplastics obtained by carrying out the polymerization of the eight or more C [which has an olefin system unsaturated bond among the decomposition oil fractions of petroleum naphtha] aromatic hydrocarbon under catalyst existence, and has the description of excelling in compatibility with various elastomers. However, C9 system petroleum resin has the fault that a color tone is bad and inferior in respect of thermal stability and weatherability.

[0003] The fault of this C9 system petroleum resin can improve by hydrogenating C9 system petroleum resin. Namely, an initial color tone is water white resin below 200 HAZEN extent, and, as for C9 system hydrogenation petroleum resin obtained by hydrogenating using the hydrogenation catalyst containing metals, such as the cobalt generally known in C9 system petroleum resin, nickel, palladium, platinum, a ruthenium, and a rhodium, a color tone, thermal stability, weatherability, etc. are greatly improved compared with non-hydrogenated C9 system petroleum resin.

[0004] However, even if it was C9 system hydrogenation petroleum resin with which a color tone, thermal stability, weatherability, etc. have been improved, in the application as which the color tone of the tackifier for hot melt adhesive used for hygienic goods, such as a disposable diaper and a sanitary napkin, etc. and especially heating stability (heat-tinting nature) are requested, it was supposed that a color tone and heating stability were still inadequate. That is, that to which C9 system hydrogenation petroleum resin used for hygienic goods etc. stopped the rate of hydrogenation of a ring from the point of compatibility with an SBS block copolymer etc. to about 5 - 80% is required, and, moreover, an initial color tone is 30 or less HAZEN. Although it is desirable that they are 3 or less Gardner as for the color tone after the 24-hour progress in 180 degrees C concerning heating stability, the initial color tone of C9 system hydrogenation petroleum resin which stopped and manufactured the rate of hydrogenation of a ring to about 5 - 80% using the well-known catalyst conventionally was 5 Gardner extent about 50 HAZEN extent and heating stability.

[0005]

[Problem(s) to be Solved by the Invention] This invention aims at offering the approach of manufacturing C9 system hydrogenation petroleum resin with good color tone and heating stability, also when the rate of hydrogenation of the ring of C9 system petroleum resin is stopped to about 5 - 80% and it hydrogenates.

[0006]

[Means for Solving the Problem] It comes to contain nickel and diatomaceous earth, as a result

of repeating examination wholeheartedly that this invention persons should solve said technical problem as a principal component. And more than 48 % of the weight or more of nickel contents, and catalyst surface area of $290\text{m}^2 / \text{g}$ And when the hydrogenation catalyst which fulfills conditions with a bulk specific gravity of $0.35\text{g} / \text{ml}$ or less has high hydrogenation activity and hydrogenation decolorization activity to C9 system petroleum resin and hydrogenates C9 system petroleum resin under existence of the hydrogenation catalyst concerned It found out that C9 system hydrogenation petroleum resin which is excellent in a color tone and heating thermal stability could be obtained. This invention is completed based on the starting new knowledge.

[0007] Namely, this invention is set to the approach of hydrogenating C9 system petroleum resin under existence of a hydrogenation catalyst, and manufacturing C9 system hydrogenation petroleum resin. As a hydrogenation catalyst, it comes to contain nickel and diatomaceous earth. 48 % of the weight or more of and nickel contents, To more than catalyst surface area of $290\text{m}^2 / \text{g}$ and the manufacture approach of C9 system hydrogenation petroleum resin characterized by using what fulfills conditions with a bulk specific gravity of $0.35\text{g} / \text{ml}$ or less, and a pan It is related with the hydrogenation catalyst of C9 system petroleum resin which comes to contain the nickel and diatomaceous earth which are used for the manufacture approach concerned, and fulfills conditions with a bulk specific gravity of $0.35\text{g} / \text{ml}$ or less more than 48 % of the weight or more of nickel contents, and catalyst surface area of $290\text{m}^2 / \text{g}$.

[0008]

[Embodiment of the Invention] Although not limited especially as C9 system petroleum resin used as the raw material of this invention, what was obtained by generally carrying out the cationic polymerization of the C9 fractions (for example, styrene, vinyltoluene, alpha methyl styrene, and indenenes etc.) obtained according to cracking of naphtha can be used. Especially the polymerization nature monomer presentation in C9 fraction can use the general thing which is not limited, for example, contains 20 - 50 % of the weight of indene content, and about 20 - 50% of vinyltoluene content, and also can also use that to which the indene content in C9 fraction was suitably reduced by distillation etc. In addition, in C9 fraction which becomes the raw material of C9 system petroleum resin here, the monomer in which a polymerization besides C5 fraction, a DCPD (dicyclopentadiene) fraction, a terpene system fraction, other styrene, and alpha methyl styrene is possible may be contained to the C9 above-mentioned fraction in the range which does not exceed 50 % of the weight. Moreover, C9 system petroleum resin may denaturalize by polar groups, such as a hydroxyl group and an ester group.

[0009] Although the softening temperature of C9 system petroleum resin and especially molecular weight are not limited, as for 70 degrees C - about 170 degrees C and number average molecular weight, 300 to about 3000 are usually desirable. The color tone of C9 system petroleum resin is usually 5 - 15 Gardner extent.

[0010] The manufacture approach of C9 system hydrogenation petroleum resin of this invention adjusts hydrogenation conditions suitably under existence of the specific hydrogenation catalyst which shows below said C9 system petroleum resin which is a raw material, and usually hydrogenates all of the olefin nature double bonds of C9 system petroleum resin, and 5% or more of a ring. If the tackifier of the rubber system hot melt adhesive which is a practical application, or ethylene-vinylacetate copolymer system hot melt adhesive is especially presented with C9 system hydrogenation petroleum resin, it will be desirable to set up the rate of hydrogenation of a ring to 40 - 80% from the point of compatibility with the base resin of adhesives.

[0011] As a hydrogenation catalyst, it is the catalyst which uses nickel and diatomaceous earth as a principal component, and more than 48 % of the weight or more of nickel contents, catalyst surface area of $290\text{m}^2 / \text{g}$, and the thing that fills the bulk specific gravity of $0.35\text{g} / \text{ml}$ or less are used. It is the catalyst which uses nickel and diatomaceous earth as a principal component, and the catalyst with which are satisfied of the above-mentioned specific conditions can discover the high hydrogenation activity of the catalyst itself, and both hydrogenation decolorant high properties to C9 system petroleum resin.

[0012] That is, the nickel content in a catalyst is determined that he wants to make high hydrogenation activity discovered, and a nickel content does not discover activity with them at 48 % of the weight. [there are few amounts of nickel which are the active spot, and sufficient]

Although especially the upper limit of a nickel content is not limited, 48 % of the weight – about 60 % of the weight is more desirable than an economical viewpoint. Catalyst surface area fully distributes nickel in a catalyst, since it fully demonstrates hydrogenation activity, it is determined by it, and catalyst surface area cannot fully discover hydrogenation decolorant by under 290m² / g. Although especially the upper limit of catalyst surface area is not restricted, it usually considers as 290–330m² / g grade. If it is determined in order to make good dispersibility of the catalyst particle in the hydrogenation system of reaction, and the bulk specific gravity of a catalyst exceeds ml in 0.35g / , the weight of a catalyst particle becomes heavy, hydrogenation activity will fall or the bulk specific gravity of a catalyst will become inadequate [hydrogenation decolorant]. Although especially the minimum of the bulk specific gravity of a catalyst is not restricted, it is usually carried out in 0.20–0.35g/ml.

[0013] Although the clear cause that the color tone and heat-tinting nature of C9 system hydrogenation petroleum resin hydrogenated using the hydrogenation catalyst of this invention are improved compared with the conventional technique is not certain, it is presumed that the coloring (heating) causative agent received hydrogenation or hydrocracking more strongly, and was achromatized in the system of reaction by the high-distributed high (based on low bulk density) active hydrogen-ized catalyst.

[0014] In addition, although the hydrogenation catalyst of this invention becomes as a principal component, nickel and diatomaceous earth The need is accepted. As a co-catalyst 1 group metals, such as sodium and a potassium, 3 group metals, such as 2 group metals, such as magnesium, calcium, and barium, and aluminum, Various kinds of things, such as metallic compounds, such as 12 group metals, such as 11 group metals, such as 9 group metals, such as 8 group metals, such as 6 group metals, such as chromium and molybdenum, and iron, and cobalt, and copper, and zinc, or these oxides, and a sulfide, can be used. A co-catalyst has the role which contributes to prehension of catalyst poison, and accommodation of the degree of surface solid acid nature, consequently controls a hydrocracking reaction.

[0015] Although especially the conditions of a hydrogenation reaction are not restricted, as for the range whose hydrogen partial pressure is 4.9 – 29.4MPa extent, and reaction temperature, it is desirable to carry out by adjusting suitably in about 240–320 degrees C. As for a hydrogen partial pressure, it is more desirable to be referred to as 14.7 or more MPas and 24.5 MPas or less, and, as for reaction temperature, it is more desirable to consider as 250 degrees C or more and 300 degrees C or less. When a hydrogen partial pressure does not fulfill 4.9MPa(s), or when reaction temperature does not fulfill 240 degrees C, a hydrogenation reaction cannot progress easily. There is not only an inclination for a hydrocracking reaction to become preferential on the other hand when a hydrogen partial pressure exceeds 29.4MPa(s), or when reaction temperature exceeds 320 degrees C, and for the fall of the softening temperature of C9 system hydrogenation petroleum resin obtained and the yield of C9 system hydrogenation petroleum resin to fall, but there is a problem in the field of the safety of a facility.

[0016] Whichever in the condition of having dissolved in the melting condition or the solvent is sufficient as the condition of the reaction of C9 system petroleum resin of a raw material. Although not limited especially as a solvent which can be used, a cyclohexane, a decalin, n-hexane, n-heptane, etc. are raised.

[0017] The amount of catalysts in a hydrogenation reaction is an amount which usually becomes 0.4 or more and 3 % of the weight or less preferably about 0.2 to 4% of the weight to C9 system petroleum resin of a raw material. When not filling the amount of the catalyst used to 0.2%, a hydrogenation reaction cannot advance easily, and when exceeding 4 % of the weight, it becomes disadvantageous in respect of cost. Moreover, reaction time is 2 hours or more and 8 hours or less preferably for about 1 to 10 hours. When not filling reaction time in 1 hour, a hydrogenation reaction cannot advance easily, and when exceeding 10 hours, it becomes disadvantageous in respect of cost.

[0018] As a reaction format of a hydrogenation reaction, either a batch process or a circulation type is employable. When using a circulation type hydrogenation reactor like especially a suspension bubbling tower, the function of the hydrogenation catalyst of this invention is demonstrated and a difference with the conventional catalyst becomes clearer. This will be

considered because the property is reflected in the reaction format if the bulk density of the hydrogenation catalyst of this invention is lighter than the conventional thing.

[0019] In this way, the softening temperature of obtained C9 system hydrogenation petroleum resin is usually about 60–170 degrees C. Softening temperatures are 70 degrees C or more and 140 degrees C or less preferably. Moreover, number average molecular weight is usually 250 to about 3000, and is 500 or more and 1500 or less preferably.

[0020]

[Effect of the Invention] According to the manufacture approach of this invention, C9 system hydrogenation petroleum resin which is excellent in a color tone and heating stability is obtained from C9 system petroleum resin. It is effective, when the rate of hydrogenation of the ring of C9 system petroleum resin is stopped to about 5 – 80% and it hydrogenates especially. That is, also after according to the manufacture approach of this invention obtaining C9 system hydrogenation petroleum resin of 30 or less HAZEN of color tones and heating obtained C9 system hydrogenation petroleum resin in 180 degrees C for 24 hours, a color tone is 3 or less Gardner, and is excellent in heating stability. Moreover, the hydrogenation catalyst used for the manufacture approach of this invention is high activity, and can reduce the catalyst expense (cost of materials) concerning hydrogenation.

[0021]

[Example] Although an example and the example of a comparison are raised to below and this invention is further explained to a detail, this invention is not limited to these examples. In addition, each section is weight criteria among each example.

[0022] Example 1 C9 system petroleum resin (as a trade name "PETOROJIN 120", color tone 10 Gardner, 120 degrees C of softening temperatures, and a principal component) The shaking type autoclave performed the hydrogenation reaction for the catalyst (49 % of the weight [of nickel contents], catalyst surface area of 292m² / g, bulk specific gravity of 0.30g/ml) 0.4 section which carried out hydrogen reduction of the 400 degrees C of the nickel-diatomaceous earth catalyst oxides which prepared vinyltoluene 30% and indene 30% with content, the 100 by Mitsui Chemicals, Inc. section, and settling under the hydrogen air current for 1 hour under hydrogen partial pressure 19.6MPa, the reaction temperature of 285 degrees C, and conditions of reaction-time 5 hours. The obtained resin was dissolved in the cyclohexane 400 section after reaction termination, and filtration removed the catalyst. Then, the filtrate was put into the separable flask of 1 liter capacity with which an impeller, the capacitor, the thermometer, the temperature controller, and the pressure display meter were attached, a temperature up and reduced pressure of were gradually done to 200 degrees C and 20torr, the solvent was removed, and 100% of rates of hydrogenation of an olefin, 60% of rates of hydrogenation of a ring, 100 degrees C of softening temperatures, and the C9 system hydrogenation petroleum resin 99 section of color tone 20 HAZEN were obtained. Moreover, the color tones (this color tone is hereafter called heating stability test) after putting 30g of obtained C9 system hydrogenation petroleum resin into the mayonnaise bottle of 70ml ** and heating at 180 degrees C in the dryer of the ** style for 24 hours were 2 Gardner. A result is shown in Table 1.

[0023] In addition, the rate of hydrogenation is raw material resin and obtained hydrogenation resin. Based on the following formulas, it computed from H-spectrum area of the ring which appears H-spectrum area and near 7 ppm the olefin which appear near 5.6 ppm in 1 H-NMR. Rate = of hydrogenation {1-(spectrum area of spectrum area / raw material resin of hydrogenation resin)} x100 (%). Moreover, softening temperature is based on the ring and ball method of JIS K 2531.

[0024] It sets in the example 2 example 1, and is C9 system petroleum resin (as a trade name "the neo polymer 120", color tone 10 Gardner, 120 degrees C of softening temperatures, and a principal component), Content and the product made of Japanese Synthetic resin are used for vinyltoluene 30% and indene 30%. As a catalyst The nickel-diatomaceous earth catalyst oxide prepared with settling under a hydrogen air current 400 degrees C, the catalyst (51 % of the weight of nickel contents, and catalyst surface area of 315m² / g --) which carried out hydrogen reduction for 1 hour The 1 section of bulk specific gravity of 0.32g/ml was used, and also the same actuation as an example 1 was performed, and 100% of rates of hydrogenation of

an olefin, 98% of rates of hydrogenation of a ring, 100 degrees C of softening temperatures, and the C9 system hydrogenation petroleum resin 101 section of color tone 20 HAZEN were obtained. Moreover, the color tone of a heating stability test was 1 Gardner. A result is shown in Table 1.

[0025] C9 system petroleum resin (the trade name "PETOROJIN 120", Mitsui Chemicals, Inc. make) and 10% catalyst slurry liquid (as what contained 10% of catalysts decalin 90%, and a catalyst) which were fused at 200 degrees C from the reactor pars basilaris ossis occipitalis in the fluid bed hydrogenation reaction container with a diameter [example 3 / of 2 inches], and a height of 1m Feed of the use was carried out for the catalyst (49 % of the weight of nickel contents, catalyst surface area of 292m² / g, bulk specific gravity of 0.30g/ml) which carried out hydrogen reduction of the 400 degrees C of the nickel-diatomaceous earth catalyst oxides prepared in ***** under the hydrogen ambient atmosphere for 1 hour with the plunger pump. Rates were a C9 system petroleum resin:360g/hour and a catalyst slurry liquid:25g/hour, respectively. The reaction condition was set as hydrogen pressure force 19.6MPa, hydrogen quantity-of-gas-flow 165 NL/H, and the reaction temperature of 280 degrees C. Reaction time (resin residence time) was about 5.5 hours. 100g of obtained C9 system hydrogenation petroleum resin was taken, and filtration removal of the catalyst was carried out after dissolving in cyclohexane 300ml. Vacuum distillation of the obtained C9 system hydrogenation petroleum resin varnish was carried out, and the cyclohexane and the decalin were distilled off. Consequently, 100g of transparent and colorless C9 system hydrogenation petroleum resin was obtained. In addition, final reduced pressure conditions were 240 degrees C, 10torr, and 20 minutes. They were 100% of rates of hydrogenation of the olefin of the obtained resin, 65% of rates of hydrogenation of a ring, 101 degrees C of softening temperatures, and color tone 20 HAZEN. Moreover, the color tones of a heating stability test were 2 Gardner. A result is shown in Table 1.

[0026] Set in the example 4 example 1. As a nickel-diatomaceous earth catalyst, it is a trade name "G-96D" (49 % of the weight of nickel contents). Used catalyst surface area of 302m² / g, a nickel-diatomaceous earth catalyst with a bulk specific gravity of 0.30g /ml], and the 0.4 sections of products made from Nissan Gar DORA Catalyst, and also the same actuation as an example 1 is performed. 100% of rates of hydrogenation of an olefin, 62% of rates of hydrogenation of a ring, 100 degrees C of softening temperatures, and the C9 system hydrogenation petroleum resin 100 section of color tone 20 HAZEN were obtained. Moreover, the color tones of a heating stability test were 2 Gardner. A result is shown in Table 1.

[0027] It sets in the example of comparison 1 example 1, and is settling as a nickel-diatomaceous earth catalyst. The 0.9 sections (42 % of the weight [of nickel contents] and catalyst surface area 187m²/g, bulk specific gravity of 0.36g/ml) of catalysts which carried out hydrogen reduction of the 400 degrees C of the prepared nickel diatomaceous earth catalyst oxides under the hydrogen air current for 1 hour were used, and also the same actuation as an example 1 was performed, and 100% of rates of hydrogenation of an olefin, 60% of rates of hydrogenation of a ring, 100 degrees C of softening temperatures, and the C9 system hydrogenation petroleum resin 101 section of color tone 50 HAZEN were obtained. Moreover, the color tones of a heating stability test were 6 Gardner. A result is shown in Table 1.

[0028] example of comparison 2 example 3 -- setting -- as catalyst slurry liquid -- 15% catalyst slurry liquid (as what contained 15% of catalysts decalin 85%, and a catalyst -- settling) Use was used for the catalyst (42 % of the weight [of nickel contents], and catalyst surface area 187m²/g, bulk specific gravity of 0.36g/ml) which carried out hydrogen reduction of the 400 degrees C of the prepared nickel diatomaceous earth catalyst oxides under the hydrogen ambient atmosphere for 1 hour, and also the same actuation as an example 3 was performed, and 100% of rates of hydrogenation of an olefin, 65% of rates of hydrogenation of a ring, 102 degrees C of softening temperatures, and the C9 system hydrogenation petroleum resin 101 section of color tone 50 HAZEN were obtained. Moreover, the color tones of a heating stability test were 6 Gardner. A result is shown in Table 1.

[0029]

[Table 1]

	触媒量 対樹脂 (%)	軟化点 (℃)	芳香環の 水素化率 (%)	C9系水素化石油樹脂	
				色調 (ハーゼン)	加熱安定性試験 (ガードナー)
実施例 1	0.4	100	60	20	2
実施例 2	1.0	100	98	20	1
実施例 3	0.7	101	65	20	2
実施例 4	0.4	100	62	20	2
比較例 1	0.9	100	60	50	6
比較例 2	1.0	102	65	50	6

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the manufacture approach of C9 system hydrogenation petroleum resin. C9 system hydrogenation petroleum resin obtained by this invention has a color tone and good thermal stability, and they can use it for tackifiers, such as encapsulant of ** and adhesives, a coating, printing ink, traffic marking paint, and a semi-conductor, a waterproof grant agent, and a pan at a plastics modifier etc.

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PRIOR ART

[Description of the Prior Art] C9 system petroleum resin is thermoplastics obtained by carrying out the polymerization of the eight or more C [which has an olefin system unsaturated bond among the decomposition oil fractions of petroleum naphtha] aromatic hydrocarbon under catalyst existence, and has the description of excelling in compatibility with various elastomers. However, C9 system petroleum resin has the fault that a color tone is bad and inferior in respect of thermal stability and weatherability.

[0003] The fault of this C9 system petroleum resin can improve by hydrogenating C9 system petroleum resin. Namely, an initial color tone is water white resin below 200 HAZEN extent, and, as for C9 system hydrogenation petroleum resin obtained by hydrogenating using the hydrogenation catalyst containing metals, such as the cobalt generally known in C9 system petroleum resin, nickel, palladium, platinum, a ruthenium, and a rhodium, a color tone, thermal stability, weatherability, etc. are greatly improved compared with non-hydrogenated C9 system petroleum resin.

[0004] However, even if it was C9 system hydrogenation petroleum resin with which a color tone, thermal stability, weatherability, etc. have been improved, in the application as which the color tone of the tackifier for hot melt adhesive used for hygienic goods, such as a disposable diaper and a sanitary napkin, etc. and especially heating stability (heat-tinting nature) are requested, it was supposed that a color tone and heating stability were still inadequate. That is, that to which C9 system hydrogenation petroleum resin used for hygienic goods etc. stopped the rate of hydrogenation of a ring from the point of compatibility with an SBS block copolymer etc. to about 5 - 80% is required, and, moreover, an initial color tone is 30 or less HAZEN. Although it is desirable that they are 3 or less Gardner as for the color tone after the 24-hour progress in 180 degrees C concerning heating stability, the initial color tone of C9 system hydrogenation petroleum resin which stopped and manufactured the rate of hydrogenation of a ring to about 5 - 80% using the well-known catalyst conventionally was 5 Gardner extent about 50 HAZEN extent and heating stability.

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EFFECT OF THE INVENTION

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] This invention aims at offering the approach of manufacturing C9 system hydrogenation petroleum resin with good color tone and heating stability, also when the rate of hydrogenation of the ring of C9 system petroleum resin is stopped to about 5 - 80% and it hydrogenates.

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MEANS

[Means for Solving the Problem] It comes to contain nickel and diatomaceous earth, as a result of repeating examination wholeheartedly that this invention persons should solve said technical problem as a principal component. And more than 48 % of the weight or more of nickel contents, and catalyst surface area of 290m² / g And when the hydrogenation catalyst which fulfills conditions with a bulk specific gravity of 0.35g [/ml] or less has high hydrogenation activity and hydrogenation decolorization activity to C9 system petroleum resin and hydrogenates C9 system petroleum resin under existence of the hydrogenation catalyst concerned It found out that C9 system hydrogenation petroleum resin which is excellent in a color tone and heating thermal stability could be obtained. This invention is completed based on the starting new knowledge.

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[0008]

[Embodiment of the Invention] Although not limited especially as C9 system petroleum resin used as the raw material of this invention, what was obtained by generally carrying out the cationic polymerization of the C9 fractions (for example, styrene, vinyltoluene, alpha methyl styrene, and indenenes etc.) obtained according to cracking of naphtha can be used. Especially the polymerization nature monomer presentation in C9 fraction can use the general thing which is not limited, for example, contains 20 - 50 % of the weight of indene content, and about 20 - 50% of vinyltoluene content, and also can also use that to which the indene content in C9 fraction was suitably reduced by distillation etc. In addition, in C9 fraction which becomes the raw material of C9 system petroleum resin here, the monomer in which a polymerization besides C5 fraction, a DCPD (dicyclopentadiene) fraction, a terpene system fraction, other styrene, and alpha methyl styrene is possible may be contained to the C9 above-mentioned fraction in the range which does not exceed 50 % of the weight. Moreover, C9 system petroleum resin may denaturalize by polar groups, such as a hydroxyl group and an ester group.

[0009] Although the softening temperature of C9 system petroleum resin and especially molecular weight are not limited, as for 70 degrees C - about 170 degrees C and number average molecular weight, 300 to about 3000 are usually desirable. The color tone of C9 system petroleum resin is usually 5 - 15 Gardner extent.

[0010] The manufacture approach of C9 system hydrogenation petroleum resin of this invention adjusts hydrogenation conditions suitably under existence of the specific hydrogenation catalyst which shows below said C9 system petroleum resin which is a raw material, and usually hydrogenates all of the olefin nature double bonds of C9 system petroleum resin, and 5% or more

of a ring. If the tackifier of the rubber system hot melt adhesive which is a practical application, or ethylene-vinylacetate copolymer system hot melt adhesive is especially presented with C9 system hydrogenation petroleum resin, it will be desirable to set up the rate of hydrogenation of a ring to 40 – 80% from the point of compatibility with the base resin of adhesives.

[0011] As a hydrogenation catalyst, it is the catalyst which uses nickel and diatomaceous earth as a principal component, and more than 48 % of the weight or more of nickel contents, catalyst surface area of $290\text{m}^2 / \text{g}$, and the thing that fills the bulk specific gravity of $0.35\text{g}/\text{ml}$ or less are used. It is the catalyst which uses nickel and diatomaceous earth as a principal component, and the catalyst with which are satisfied of the above-mentioned specific conditions can discover the high hydrogenation activity of the catalyst itself, and both hydrogenation decolorant high properties to C9 system petroleum resin.

[0012] That is, the nickel content in a catalyst is determined that he wants to make high hydrogenation activity discovered, and a nickel content does not discover activity with them at 48 % of the weight. [there are few amounts of nickel which are the active spot, and sufficient] Although especially the upper limit of a nickel content is not limited, 48 % of the weight – about 60 % of the weight is more desirable than an economical viewpoint. Catalyst surface area fully distributes nickel in a catalyst, since it fully demonstrates hydrogenation activity, it is determined by it, and catalyst surface area cannot fully discover hydrogenation decolorant by under $290\text{m}^2 / \text{g}$. Although especially the upper limit of catalyst surface area is not restricted, it usually considers as $290\text{--}330\text{m}^2 / \text{g}$ grade. If it is determined in order to make good dispersibility of the catalyst particle in the hydrogenation system of reaction, and the bulk specific gravity of a catalyst exceeds ml in $0.35\text{g} /$, the weight of a catalyst particle becomes heavy, hydrogenation activity will fall or the bulk specific gravity of a catalyst will become inadequate [hydrogenation decolorant]. Although especially the minimum of the bulk specific gravity of a catalyst is not restricted, it is usually carried out in $0.20\text{--}0.35\text{g}/\text{ml}$.

[0013] Although the clear cause that the color tone and heat-tinting nature of C9 system hydrogenation petroleum resin hydrogenated using the hydrogenation catalyst of this invention are improved compared with the conventional technique is not certain, it is presumed that the coloring (heating) causative agent received hydrogenation or hydrocracking more strongly, and was achromatized in the system of reaction by the high-distributed high (based on low bulk density) active hydrogen-ized catalyst.

[0014] In addition, although the hydrogenation catalyst of this invention becomes as a principal component, nickel and diatomaceous earth The need is accepted. As a co-catalyst 1 group metals, such as sodium and a potassium, 3 group metals, such as 2 group metals, such as magnesium, calcium, and barium, and aluminum, Various kinds of things, such as metallic compounds, such as 12 group metals, such as 11 group metals, such as 9 group metals, such as 8 group metals, such as 6 group metals, such as chromium and molybdenum, and iron, and cobalt, and copper, and zinc, or these oxides, and a sulfide, can be used. A co-catalyst has the role which contributes to prehension of catalyst poison, and accommodation of the degree of surface solid acid nature, consequently controls a hydrocracking reaction.

[0015] Although especially the conditions of a hydrogenation reaction are not restricted, as for the range whose hydrogen partial pressure is $4.9\text{--}29.4\text{MPa}$ extent, and reaction temperature, it is desirable to carry out by adjusting suitably in about $240\text{--}320$ degrees C. As for a hydrogen partial pressure, it is more desirable to be referred to as 14.7 or more MPas and 24.5 MPas or less, and, as for reaction temperature, it is more desirable to consider as 250 degrees C or more and 300 degrees C or less. When a hydrogen partial pressure does not fulfill 4.9MPa(s) , or when reaction temperature does not fulfill 240 degrees C, a hydrogenation reaction cannot progress easily. There is not only an inclination for a hydrocracking reaction to become preferential on the other hand when a hydrogen partial pressure exceeds 29.4MPa(s) , or when reaction temperature exceeds 320 degrees C, and for the fall of the softening temperature of C9 system hydrogenation petroleum resin obtained and the yield of C9 system hydrogenation petroleum resin to fall, but there is a problem in the field of the safety of a facility.

[0016] Whichever in the condition of having dissolved in the melting condition or the solvent is sufficient as the condition of the reaction of C9 system petroleum resin of a raw material.

Although not limited especially as a solvent which can be used, a cyclohexane, a decalin, n-hexane, n-heptane, etc. are raised.

[0017] The amount of catalysts in a hydrogenation reaction is an amount which usually becomes 0.4 or more and 3 % of the weight or less preferably about 0.2 to 4% of the weight to C9 system petroleum resin of a raw material. When not filling the amount of the catalyst used to 0.2%, a hydrogenation reaction cannot advance easily, and when exceeding 4 % of the weight, it becomes disadvantageous in respect of cost. Moreover, reaction time is 2 hours or more and 8 hours or less preferably for about 1 to 10 hours. When not filling reaction time in 1 hour, a hydrogenation reaction cannot advance easily, and when exceeding 10 hours, it becomes disadvantageous in respect of cost.

[0018] As a reaction format of a hydrogenation reaction, either a batch process or a circulation type is employable. When using a circulation type hydrogenation reactor like especially a suspension bubbling tower, the function of the hydrogenation catalyst of this invention is demonstrated and a difference with the conventional catalyst becomes clearer. This will be considered because the property is reflected in the reaction format if the bulk density of the hydrogenation catalyst of this invention is lighter than the conventional thing.

[0019] In this way, the softening temperature of obtained C9 system hydrogenation petroleum resin is usually about 60-170 degrees C. Softening temperatures are 70 degrees C or more and 140 degrees C or less preferably. Moreover, number average molecular weight is usually 250 to about 3000, and is 500 or more and 1500 or less preferably.

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EXAMPLE

[Example] Although an example and the example of a comparison are raised to below and this invention is further explained to a detail, this invention is not limited to these examples. In addition, each section is weight criteria among each example.

[0022] Example 1C9 system petroleum resin (as a trade name "PETOROJIN 120", color tone 10 Gardner, 120 degrees C of softening temperatures, and a principal component) The shaking type autoclave performed the hydrogenation reaction for the catalyst (49 % of the weight [of nickel contents], catalyst surface area of 292m² / g, bulk specific gravity of 0.30g/ml) 0.4 section which carried out hydrogen reduction of the 400 degrees C of the nickel-diatomaceous earth catalyst oxides which prepared vinyltoluene 30% and indene 30% with content, the 100 by Mitsui Chemicals, Inc. section, and settling under the hydrogen air current for 1 hour under hydrogen partial pressure 19.6MPa, the reaction temperature of 285 degrees C, and conditions of reaction-time 5 hours. The obtained resin was dissolved in the cyclohexane 400 section after reaction termination, and filtration removed the catalyst. Then, the filtrate was put into the separable flask of 1 liter capacity with which an impeller, the capacitor, the thermometer, the temperature controller, and the pressure display meter were attached, a temperature up and reduced pressure of were gradually done to 200 degrees C and 20torr, the solvent was removed, and 100% of rates of hydrogenation of an olefin, 60% of rates of hydrogenation of a ring, 100 degrees C of softening temperatures, and the C9 system hydrogenation petroleum resin 99 section of color tone 20 HAZEN were obtained. Moreover, the color tones (this color tone is hereafter called heating stability test) after putting 30g of obtained C9 system hydrogenation petroleum resin into the mayonnaise bottle of 70ml ** and heating at 180 degrees C in the dryer of the ** style for 24 hours were 2 Gardner. A result is shown in Table 1.

[0023] In addition, the rate of hydrogenation is raw material resin and obtained hydrogenation resin. Based on the following formulas, it computed from H-spectrum area of the ring which appears H-spectrum area and near 7 ppm the olefin which appear near 5.6 ppm in 1 H-NMR. Rate =of hydrogenation {1-(spectrum area of spectrum area / raw material resin of hydrogenation resin)} x100 (%). Moreover, softening temperature is based on the ring and ball method of JIS K 2531.

[0024] It sets in the example 2 example 1, and is C9 system petroleum resin (as a trade name "the neo polymer 120", color tone 10 Gardner, 120 degrees C of softening temperatures, and a principal component), Content and the product made of Japanese Synthetic resin are used for vinyltoluene 30% and indene 30%. As a catalyst The nickel-diatomaceous earth catalyst oxide prepared with settling under a hydrogen air current 400 degrees C, the catalyst (51 % of the weight of nickel contents, and catalyst surface area of 315m² / g --) which carried out hydrogen reduction for 1 hour The 1 section of bulk specific gravity of 0.32g/ml was used, and also the same actuation as an example 1 was performed, and 100% of rates of hydrogenation of an olefin, 98% of rates of hydrogenation of a ring, 100 degrees C of softening temperatures, and the C9 system hydrogenation petroleum resin 101 section of color tone 20 HAZEN were obtained. Moreover, the color tone of a heating stability test was 1 Gardner. A result is shown in Table 1.

[0025] C9 system petroleum resin (the trade name "PETOROJIN 120", Mitsui Chemicals, Inc.

make) and 10% catalyst slurry liquid (as what contained 10% of catalysts decalin 90%, and a catalyst) which were fused at 200 degrees C from the reactor pars basilaris ossis occipitalis in the fluid bed hydrogenation reaction container with a diameter [example 3 / of 2 inches], and a height of 1m Feed of the use was carried out for the catalyst (49 % of the weight of nickel contents, catalyst surface area of 292m² / g, bulk specific gravity of 0.30g/ml) which carried out hydrogen reduction of the 400 degrees C of the nickel-diatomaceous earth catalyst oxides prepared in ***** under the hydrogen ambient atmosphere for 1 hour with the plunger pump. Rates were a C9 system petroleum resin:360g/hour and a catalyst slurry liquid:25g/hour, respectively. The reaction condition was set as hydrogen pressure force 19.6MPa, hydrogen quantity-of-gas-flow 165 NL/H, and the reaction temperature of 280 degrees C. Reaction time (resin residence time) was about 5.5 hours. 100g of obtained C9 system hydrogenation petroleum resin was taken, and filtration removal of the catalyst was carried out after dissolving in cyclohexane 300ml. Vacuum distillation of the obtained C9 system hydrogenation petroleum resin varnish was carried out, and the cyclohexane and the decalin were distilled off. Consequently, 100g of transparent and colorless C9 system hydrogenation petroleum resin was obtained. In addition, final reduced pressure conditions were 240 degrees C, 10torr, and 20 minutes. They were 100% of rates of hydrogenation of the olefin of the obtained resin, 65% of rates of hydrogenation of a ring, 101 degrees C of softening temperatures, and color tone 20 HAZEN. Moreover, the color tones of a heating stability test were 2 Gardner. A result is shown in Table 1.

[0026] Set in the example 4 example 1. As a nickel-diatomaceous earth catalyst, it is a trade name "G-96D" (49 % of the weight of nickel contents). Used catalyst surface area of 302m² / g, a nickel-diatomaceous earth catalyst with a bulk specific gravity of 0.30g [/ml], and the 0.4 sections of products made from Nissan Gar DORA Catalyst, and also the same actuation as an example 1 is performed. 100% of rates of hydrogenation of an olefin, 62% of rates of hydrogenation of a ring, 100 degrees C of softening temperatures, and the C9 system hydrogenation petroleum resin 100 section of color tone 20 HAZEN were obtained. Moreover, the color tones of a heating stability test were 2 Gardner. A result is shown in Table 1.

[0027] It sets in the example of comparison 1 example 1, and is settling as a nickel-diatomaceous earth catalyst. The 0.9 sections (42 % of the weight [of nickel contents] and catalyst surface area 187m²/g, bulk specific gravity of 0.36g/ml) of catalysts which carried out hydrogen reduction of the 400 degrees C of the prepared nickel diatomaceous earth catalyst oxides under the hydrogen air current for 1 hour were used, and also the same actuation as an example 1 was performed, and 100% of rates of hydrogenation of an olefin, 60% of rates of hydrogenation of a ring, 100 degrees C of softening temperatures, and the C9 system hydrogenation petroleum resin 101 section of color tone 50 HAZEN were obtained. Moreover, the color tones of a heating stability test were 6 Gardner. A result is shown in Table 1.

[0028] example of comparison 2 example 3 -- setting -- as catalyst slurry liquid -- 15% catalyst <TXF FR=0002 HE=060 WI=080 LX=1100 LY=0300> slurry liquid (as what contained 15% of catalysts decalin 85%, and a catalyst -- settling) Use was used for the catalyst (42 % of the weight [of nickel contents], and catalyst surface area 187m²/g, bulk specific gravity of 0.36g/ml) which carried out hydrogen reduction of the 400 degrees C of the prepared nickel diatomaceous earth catalyst oxides under the hydrogen ambient atmosphere for 1 hour, and also the same actuation as an example 3 was performed, and 100% of rates of hydrogenation of an olefin, 65% of rates of hydrogenation of a ring, 102 degrees C of softening temperatures, and the C9 system hydrogenation petroleum resin 101 section of color tone 50 HAZEN were obtained. Moreover, the color tones of a heating stability test were 6 Gardner. A result is shown in Table 1.

[0029]

[Table 1]

	触媒量 対樹脂 (%)	軟化点 (℃)	芳香環の 水素化率 (%)	C9系水素化石油樹脂	
				色調 (ハーゼン)	加熱安定性試験 (ガードナー)
実施例 1	0.4	100	60	20	2
実施例 2	1.0	100	98	20	1
実施例 3	0.7	101	65	20	2
実施例 4	0.4	100	62	20	2
比較例 1	0.8	100	60	50	6
比較例 2	1.0	102	65	50	6

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